



# Comparative analysis on temperature swing adsorption cycle for carbon capture by using internal heat/mass recovery



L. Jiang<sup>a,\*</sup>, R.Q. Wang<sup>a</sup>, A. Gonzalez-Diaz<sup>a</sup>, A. Smallbone<sup>a</sup>, R.O. Lamidi<sup>b</sup>, A.P. Roskilly<sup>a</sup>

<sup>a</sup> School of Engineering, Durham University, Durham DH1 3LE, UK

<sup>b</sup> Sir Joseph Swan Centre for Energy Research, Newcastle University, Newcastle NE1 7RU, UK

## HIGHLIGHTS

- Performance of a 4-step TSA cycle is further explored by recovery technology.
- Unused percentage and metal part have great influence on the real performance.
- Heat recovery is conducive to TSA while mass recovery is more suitable for VSA.
- The up limit of exergy efficiencies using recovery technology could reach 40–45%.

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## ABSTRACT

Due to relatively high energy consumption of absorption technology, adsorption carbon dioxide capture is gathering the momentum in recent years. This paper aims to further improve the thermal performance of a 4-step temperature swing adsorption cycle by integrating internal mass recovery and heat recovery. Exergy efficiency is evaluated by using adsorption characteristics of activated carbon and compared in terms of four different situations i.e. basic cycle, heat recovery cycle, mass recovery cycle, heat and mass recovery cycle, which could illustrate the advantages and disadvantages of different recovery technologies. Results demonstrate that heat recovery and mass recovery technologies are quite conducive to improve the up limit of cycle thermal efficiency. Under the conditions of different desorption/adsorption temperatures and pressures, exergy efficiencies using recovery technologies could be improved by up to 2.86 times when compared with that of basic cycle. Besides, in real application unused percentage of adsorption reactor and metal ratio have large influence on the cycle performance while mass recovery rate has a relatively small influence. One potential application of the proposed recovery technologies is direct air capture in building ventilation system since a largest improvement could be achieved at a low carbon dioxide concentration.

## 1. Introduction

According to Intergovernmental Panel on Climate Change (IPCC), global temperature is predicted to increase 1.5 °C based on the pre-industrial levels between 2030 and 2052 [1]. To control atmosphere CO<sub>2</sub> level, one solution is switching fossil fuels into renewable sources with the improved energy efficiency. The other effective way is the use of capture, utilisation and storage (CCUS) technology [2,3]. Currently, oxygen-combustion, pre- and post-combustion capture are three technical ways for capturing CO<sub>2</sub> from power plants. Comparably, post-combustion has a relative small effect on the power generation which is the most investigated technology [4,5]. A variety of methods e.g. cryogenic, membrane, adsorption, absorption process could achieve the

post-combustion carbon capture [6,7]. Among these methods, absorption technology using amine based solution e.g. monoethanolamine (MEA) could reach a commercial scale and is currently the most mature approach for capturing CO<sub>2</sub> from power plants [8,9]. Lots of demonstration projects could be found in the recent years [10]. Nonetheless, the main disadvantages are that MEA is corrosive and consumes a large amount of energy during the regeneration process. Also it produces other components e.g. formaldehyde and various kinds of acid that cannot be regenerated by thermal heat which will inevitably reduce the usable efficiency of the reactor [11]. Compared with liquid absorption candidates for CO<sub>2</sub> capture, solid adsorption is always regarded as a counterpart technology that has been extensively studied in the field of thermal energy storage, refrigeration and power generation

\* Corresponding author.

E-mail address: [Long.jiang@durham.ac.uk](mailto:Long.jiang@durham.ac.uk) (L. Jiang).

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Nomenclature		Greek letters	
A	adsorption potential ( $\text{J}\cdot\text{mol}^{-1}$ )	$\eta$	efficiency
AC	activated carbon	$\psi$	percentage
CCUS	carbon capture, utilisation and storage	$\varphi$	mass ratio between reactor and adsorbent
$C_p$	specific heat capacity ( $\text{kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ )	$\varepsilon$	mass recovery rate
DAC	direct air capture		
E	characteristics energy ( $\text{J}\cdot\text{mol}^{-1}$ )	<i>Subscripts</i>	
ESA	electric swing adsorption	a	adsorbent
H	reaction heat ( $\text{kJ}\cdot\text{kg}^{-1}$ )	$\text{CO}_2$	carbon dioxide
IHR	internal heat recovery	c	cooling
IHMR	internal heat and mass recovery	de	desorption
IMR	internal mass recovery	e	evaporation
IPCC	intergovernmental panel on climate change	ex	exergy
M	mass (kg)	H	high temperature
MOF	metal organic framework	L	low temperature
MEA	monoethanolamine	hr	heat recovery
P	pressure (Pa)	In	input
PSA	pressure swing adsorption	i	ideal
PTSA	pressure-temperature swing adsorption	m	medium
Q	heat (kJ)	ma	mass
q	$\text{CO}_2$ adsorption capacity ( $\text{mg}\cdot\text{kg}^{-1}$ )	min	minimum
$\text{Re}_{\text{CO}_2}$	$\text{CO}_2$ recovery (%)	mr	mass recovery
T	temperature ( $^{\circ}\text{C}$ )	R	reaction
TSA	temperature swing adsorption	r	real
VSA	vacuum swing adsorption	re	reactor
$v_a$	specific volume of the liquid adsorbate	S	input shaft work
W	work ( $\text{kJ}\cdot\text{kg}^{-1}$ )	s	sensible
WC	working capacity ( $\text{kg}\cdot\text{kg}^{-1}$ )	un	unusage
$y_{\text{CO}_2}$	$\text{CO}_2$ concentration		

[12,13]. Solid adsorbents generally do not pose any health hazard and they can avoid the evaporation of water in the regeneration stage which results in a relatively smaller energy consumption than that of absorption technology [14].

Cyclic operation of adsorption  $\text{CO}_2$  capture could be divided into adsorption and desorption steps, which form different thermal cycles. The most common adsorption cycles are pressure swing adsorption (PSA) and temperature swing adsorption (TSA). The main demarcation line relies on the treatment of desorption processes. The adsorbed gases for TSA are desorbed after adsorption steps by heating the adsorbent while the pressure of adsorbent in PSA is reduced for creating the potential for desorption. If the pressure is lower than atmosphere, vacuum pressure swing adsorption (VSA) is termed as another type of PSA [15]. Due to low grade heat utilisation, TSA is quite attractive among adsorption carbon capture technologies. Another reason is that PSA is predicted to be more costly than heating the solid material [15]. Based on carbon pump concept proposed recently, exergy efficiencies of carbon capture cycle could be evaluated for comparison. Therefore, a thermal cycle with a higher exergy efficiency reveals more potentials to reduce the energy penalty. In our previous work, analogy is used to compare adsorption refrigeration cycle with adsorption carbon capture cycle. Exergy efficiency of a 4-step TSA cycle is further improved by using internal heat recovery (IHR) [16]. It is acknowledged that heat recovery and mass recovery are independent and interdependent when considering adsorption cycles. Different recovery technologies would play different roles in regeneration heat and cycle performance. Comparably, internal mass recovery (IMR) is to recover additional mass adsorption capacities between the reactors [17]. Li et al. [18] conducted the entropy analysis on the thermodynamic cycle by using IHR and indicated the importance of the heat recovery technology. This study also indicated the potential of pressure difference which proved the significance of the IMR from another perspective [18]. Although small heat transfer happens during the mass recovery process, it doesn't

change the basic concept of IMR. IHR and IMR target different temperature and pressure potentials, which respectively reduce the regeneration heat per mass of  $\text{CO}_2$ . In the end of our recent work, a novel design was proposed for a TSA system by using internal heat and mass recovery (IHMR) tank. However, cycle performance of  $\text{CO}_2$  capture by using IHMR had not been analysed. The core problems are not ensured i.e. whether IMR/IHMR is useful and how effective it is to adsorption carbon capture, which are quite interesting to give the answer in this paper.

In general, diverse classes of adsorbents have been identified for  $\text{CO}_2$  capture technology, which are mainly divided into physical and chemical adsorbents according to their reaction driving force [19,20]. Chemical adsorbents usually have higher sorption capacities and relative high regeneration temperatures when compared with those characteristics of physical adsorbents [21]. The main chemical sorbents are amine-based sorbents. However, chemical adsorbents also have some drawbacks e.g. degradation caused by the reaction with oxygen and the causticity which may result in some barriers like maintenance in the real application [22]. Due to the potentials of high selectivity, large sorption capacity and relatively low regeneration heat, metal-organic framework (MOF) could combine advantages of both physical and chemical adsorbents, which has set off a research boom in the past few years [23]. A comprehensive analysis of 11 types of the adsorbents has been conducted and it indicated that Mg-MOF-74 was a prospective material that could be used in TSA technology for post combustion carbon capture [24]. The main drawback is that the cost of MOF cannot be further reduced to the cheap price as other sorbents e.g. AC and zeolite. Besides, kinetics of AC and zeolite in the adsorption and desorption processes have been investigated by various research studies. Hence, their properties could be available to be used for further evaluation of different applications, which will give more general insights and inspirations when compared with those adsorbents that have the higher sorption performance [25,26].

This paper aims to appraise the performance of a 4-step TSA cycle by using IMR for CO<sub>2</sub> capture, which has not been covered in any literature. The main novelties mainly lie in up limit exploration of cycle performance, three key parameters in real application and a potential application proposed in terms of different recovery technologies. Besides, AC is selected as the adsorbent, which is used to compare the performance with that using IHR in our previous work. Regeneration heat and exergy efficiency are then determined in terms of various adsorption/desorption temperatures and pressures. Cycle performance with IHR, IMR and IHMR will be analysed separately and compared with that of the basic cycle for further illustrating their advantages and disadvantages. The framework of this paper is illustrated as follows. The novel cycle is introduced in Section 2 where working principles of adsorption cycles are illustrated. Then methodology applied in the study is presented in Section 3. Section 4 presents the results and discussions followed by conclusions in Section 5.

## 2. Working principles of adsorption cycles for carbon capture

The general schematic diagram of a basic 4-step TSA cycle is shown in Fig. 1 which is depicted by using fixed reactors according to carbon pump theory based on the following assumptions [27].

- (1) Temperature inside the adsorbent is uniform by considering the equilibrium performance, i.e. no temperature gradient happens in different directions. This is mainly because performance analysis of thermodynamic cycle is the main research target rather than real reaction.
- (2) CO<sub>2</sub> is the main adsorbate in adsorbent when compared with other adsorbates e.g. N<sub>2</sub>, water which can be neglected.
- (3) CO<sub>2</sub> is evenly distributed in adsorber and sorbent material during each adsorption and desorption process of the TSA cycle.

A basic 4-step TSA cycle is composed of four working processes i.e. adsorption, preheating, desorption and precooling. The details of each step could refer to our previous work [16]. Thus, it is briefly illustrated according to Fig. 1 as follows:

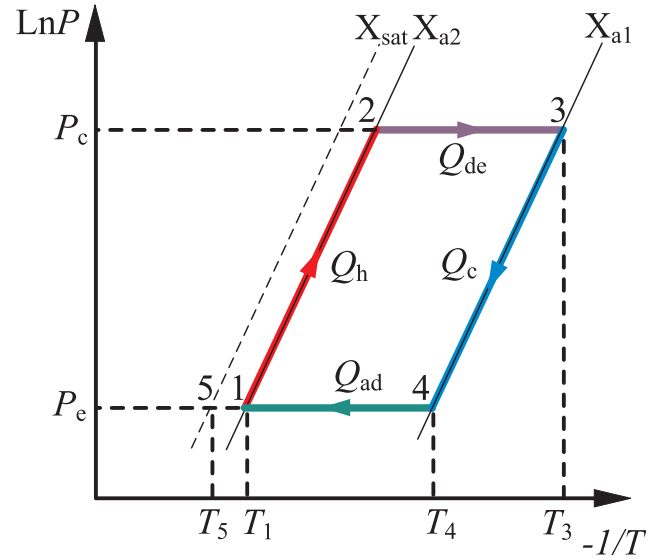


Fig. 2. Clapeyron diagram of a 4-step TSA cycle for CO<sub>2</sub> capture.

Step 1-2 is an adsorption process. During this process, gas mixture flows into the adsorption reactor. Then CO<sub>2</sub> is adsorbed by the adsorbent, and reaction heat is removed by cooling water. Theoretical adsorption process could reach point 5 but cannot achieve that in real application.

Step 2-3 is a preheating process. Adsorption reactor is immediately heated by heating medium. Temperature of the reactor is increased but no CO<sub>2</sub> is desorbed.

Step 3-4 is a desorption process. After temperature reaching  $T_3$  at point 3, desorption process of CO<sub>2</sub> begins, and CO<sub>2</sub> with a high concentration flows out of the reactor until its temperature reaches  $T_4$ .

Step 4-1 is a precooling process. Cooling medium is used to remove the heat from adsorption reactor. The operation conditions are resumed by starting a new 4-step TSA cycle.

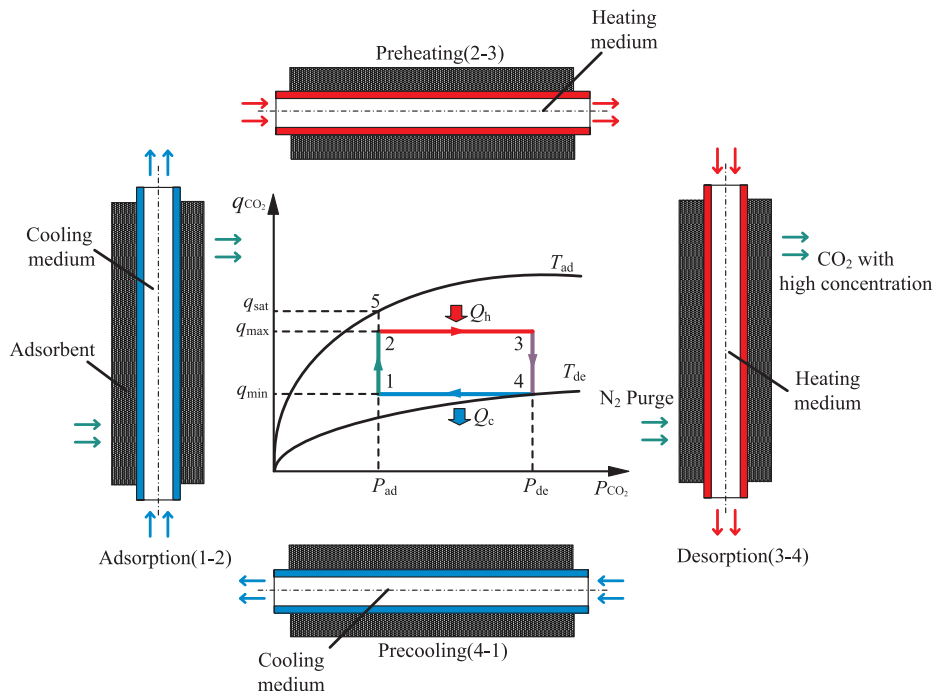


Fig. 1. Schematic diagram of a 4-step TSA cycle for CO<sub>2</sub> capture.



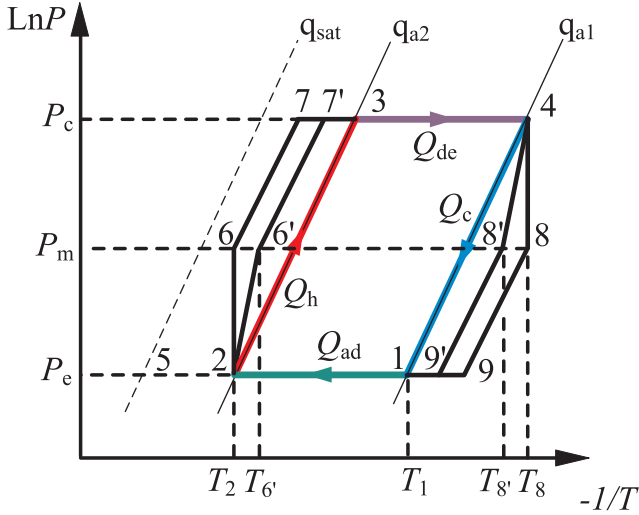


Fig. 4. The  $P$ - $T$  diagram of adsorption-based post-combustion  $\text{CO}_2$  capture using IMR.

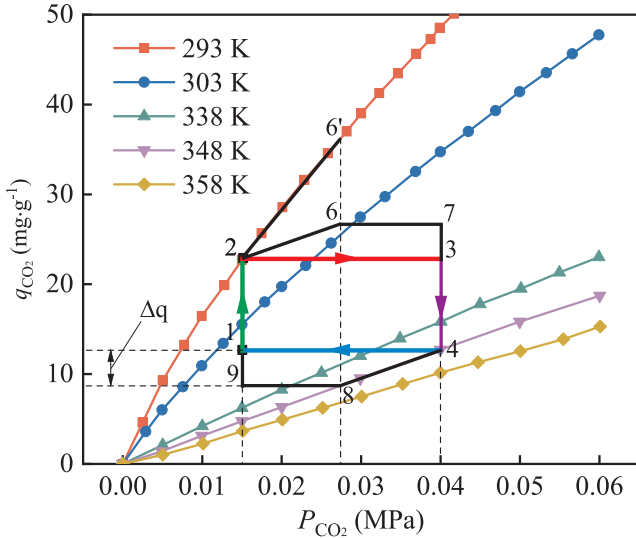


Fig. 5. Cycle characteristic of a 4-step TSA cycle using IMR based on properties of AC.

$$Q_R = (Q_{s,\text{CO}_2} + Q_{s,a} + Q_{s,\text{re}} + Q_{l,a}) / (q_2 - q_1) \\ = (Q_{s,\text{CO}_2} + Q_{s,a} + Q_{s,\text{re}}) / (q_2 - q_1) + H_a \quad (6)$$

where the first term in the right side denotes sensible heat of adsorbed  $\text{CO}_2$ , the second and third term is sensible heat of adsorbent and adsorption reactor, respectively. The fourth term is reaction heat of adsorbent.  $q_2$  and  $q_1$  are desorption capacities of point 2 and point 1 according to Fig. 1.

In this paper, IHR is analysed theoretically, which demonstrates that  $T_{\text{hr}}$  is the average value of  $T_h$  and  $T_l$ . After IHR, regeneration heat of the 4-step TSA cycle is reduced as shown in Eq. (7).

$$Q_R' = (Q_{s,\text{CO}_2} + Q_{s,a} + Q_{s,\text{re}} + Q_{s,L} - Q_{\text{hr}}) / (q_2 - q_1) \quad (7)$$

where  $Q_{\text{hr}}$  is the recovered sensible heat of adsorbent and the reactor through IHR.

For IMR, regeneration heat of 4-step TSA cycle could be further reduced as shown in Eq. (8).

$$Q_R' = (Q_{s,\text{CO}_2} + Q_{s,a} + Q_{s,\text{re}} + Q_{s,L} - Q_{\text{hr}}) / (q_2 - q_1 + \Delta q) \quad (8)$$

where  $\Delta q$  is the additional working capacity obtained from IMR.

The additional working capacity  $\Delta q$  could be defined as Eq. (9).

$$\Delta q = \Delta q_{26} = \Delta q_{48} \quad (9)$$

where the subscripts denote working state according to Fig. 4, e.g.  $\Delta q_{26}$  means the difference sorption capacity between point 4 and point 6.

In real application, the isothermal IMR cannot be achieved. Thus, the additional working capacity  $\Delta q$  could then be calculated based on Eqs. (10)–(12).

$$(C_{p,a} + C_{p,\text{CO}_2} \Delta q_{26})(T_6' - T_2) = H_a \Delta q_{26}' \quad (10)$$

$$(C_{p,a} + C_{p,\text{CO}_2} \Delta q_{48})(T_4 - T_8') = H_a \Delta q_{48}' \quad (11)$$

$$P_6' = P_8' \quad (12)$$

where  $C_{p,a}$  and  $C_{p,\text{CO}_2}$  are the specific heat of the adsorbent and adsorbed  $\text{CO}_2$ ,  $\Delta q_{26}'$  denotes the difference sorption capacity between point 2 and point 6',  $H_a$  is the reaction heat of adsorbent.

From the equations of performance analysis, it could be found that IHR and IMR aim to improve the cycle performance from different aspects, which either decrease the numerator or reduce denominator when calculating the regeneration heat.

### 3.3. Variable factors used for flexibility analysis

Thermal performance of a 4-step TSA cycle with recovery technologies could be influenced by various factors e.g. heat and mass transfer performance, unused percentage, etc. Three main variable parameters are then adopted to further illustrate the performance in real application, which are listed as follows.

It is acknowledged that the adsorption reactor could not be efficiently used due to dead volume in the system. The unused percentage of adsorption reactor ( $\psi_{\text{un}}$ ) is defined according to Eq. (13).

$$\psi_{\text{un}} = 1 - \frac{q_2}{q_5} \quad (13)$$

where  $q_1$ ,  $q_2$  and  $q_5$  are adsorption capacities of point 1, 2 and 5 in Fig. 1.

Mass ratio between mass of adsorption reactor and adsorbent ( $\varphi_{\text{ma}}$ ) is adopted as Eq. (14), which is used to evaluate its influence on IHR in real application.

$$\varphi_{\text{ma}} = \frac{M_{\text{re}}}{M_a} \quad (14)$$

where  $M_r$  and  $M_a$  are the mass of adsorption reactor and adsorbent, respectively.

Mass recovery coefficient ( $\varepsilon_{\text{mr}}$ ) is used as the real recovered mass capacity divided by ideal recovered capacity under isothermal condition. It is used to evaluate its influence on the performance of IMR in real application, which is shown as Eq. (15).

$$\varepsilon_{\text{mr}} = \frac{\Delta q_r}{\Delta q_i} \quad (15)$$

where  $\Delta q_r$  and  $\Delta q_i$  are real and ideal additional working capacity, respectively.

## 4. Results and discussions

Theoretical performance of 4-step TSA cycles is first evaluated based on the carbon pump theory by using the characteristics of AC. Regeneration heat and exergy efficiency are two main outputs which are compared in terms of basic cycle, cycle with IHR, cycle with IMR and cycle with IHMR. Regeneration heat is defined as the specific value divided by mass of  $\text{CO}_2$  working capacity which is simplified as regeneration heat in this section. Afterwards, the unused percentage of adsorption reactor, mass ratio between adsorption reactor and adsorbent as well as mass recovery coefficient are adopted for further assessing the performance in real application.



#### 4.1. Theoretical performance

Regeneration heat and exergy efficiency of 4-step TSA cycles are presented under the conditions of the aforementioned selected desorption/adsorption temperature and pressure which are respectively indicated in Fig. 6, Fig. 7, Fig. 8 and Fig. 9. When one parameter e.g. desorption temperature varies, others i.e. desorption temperature, adsorption temperature and pressure keep the same.

As shown in Fig. 6a, regeneration heat increases with the increase of desorption pressure due to the fact that working capacity greatly decreases with the increase of desorption pressure according to Eq. (6). The recovery technologies do have great influence on the reduction of regeneration heat. IHR could be more effective at low desorption pressure whereas the cycle with IMR shows better performance at high desorption pressure. The reasons are illustrated as follows: total working capacity is relatively large when desorption pressure is low. Additional adsorption capacity caused by IMR is relatively small when compared with total working capacity which indicates a small percentage. Thus the cycle using IMR could result in a limited reduction of regeneration heat. Comparably, when the desorption pressure increases, the ratio between additional adsorption capacity and total working capacity greatly increases which improves the effect of IMR. Due to similar temperature difference between heating and cooling source, the proportion of reduction is close at different desorption pressure. Based on Eq. (5), exergy efficiency is evaluated and shows a reverse trend in Fig. 6b. Results indicate that the highest exergy efficiency of 4-step TSA cycles with recovery technologies could reach 0.465 by using IHMR at a desorption pressure of 0.03 MPa. When the desorption pressure varies from 0.03 MPa to 0.06 MPa, exergy efficiency ranges from 0.065 to 0.465. The recovery technologies could improve the efficiency up to 3.5 times when compared with the performance of basic cycle. It is feasible to realize a great improvement only using IHR at small desorption pressure. At higher desorption pressure, the highest improvement is achieved by IHMR.

As observed in Fig. 7a, with the decrease of desorption temperature, regeneration heat increases since cycle working capacity is increased. Sensible heat in regeneration heat declines while reaction heat of adsorbent increases. Also, IHR is more conducive to the regeneration heat reduction at high desorption temperature due to the large sensible heat demands that are caused by large temperature difference. Comparably, IMR is better to be used at low desorption temperature. This could also be attributed to the larger ratio between additional adsorption capacity and total working capacity. Besides, it is worth noting that exergy efficiency increases first then decreases with the increase of desorption temperature as shown in Fig. 7b. The highest exergy efficiency of 4-step TSA cycles could reach 0.438 by using IHMR at a desorption temperature of 338 K. When the desorption temperature varies from 328 K to 358 K, exergy efficiency ranges from 0.1 to 0.438. Compared with

the performance of basic cycle, the efficiency could be improved by up to 2.47 times. Combined the previous results at different desorption pressure, it is recommended to select the optimal desorption temperature and control desorption pressure as low as possible. Also, both IHR and IMR are better to be jointly used at different desorption temperatures.

Regeneration heat and exergy efficiency of 4-step TSA cycles at different adsorption pressures are presented in Fig. 8a and Fig. 8b, respectively. It is indicated that the regeneration heat could be greatly increased with the decrease of the adsorption pressure. Both IHR and IMR technologies have large influence on the cycle performance when adsorption pressure is lower than 0.15 since working capacity is also very low and improvement of regeneration heat become obvious. It is demonstrated that exergy efficiency increases from 0.072 to 0.402 when the adsorption pressure increases from 0.01 MPa to 0.02 MPa. The largest improvement by using recovery technologies could reach 2.83 times at 0.01 MPa adsorption pressure. Also worth noting that IMR has a relatively small contribution to further improve the cycle performance when compared with IHR. This is mainly because working capacity becomes large which means that the ratio between additional adsorption capacity and total working capacity cannot be further improved greatly.

Similarly, Fig. 9 shows thermal performance of 4-step TSA cycles at different adsorption temperature, in which regeneration heat and exergy efficiency are indicated in Fig. 9a and 9b, respectively. It could be observed that regeneration heat increases with the increase of adsorption temperature, and exergy efficiency shows a reverse trend. Both IHR and IMR are better to be applied when the adsorption temperature is relatively high. Results show that exergy efficiency increases from 0.072 to 0.39 when adsorption pressure increases from 293 K to 303 K. The largest improvement by using recovery technologies could reach 2.67 times at an adsorption temperature of 303 K. In real application, it is suggested to increase the adsorption pressure and reduce the adsorption temperature. However, adsorption temperature and pressure are determined by flue gas of power plant and environmental cooling medium for post-combustion CCS technology, which is not able to change greatly. Thus, IHMR could be a good solution to further improve the thermal cycle performance.

#### 4.2. Flexibility analysis for real applications

This subsection aims to investigate the influence of recovery technologies on thermal performance of the 4-step TSA cycles in real application. Three variables i.e. unused percentage of adsorption reactor, mass ratio between adsorption reactor and adsorbent as well as mass recovery coefficient are adopted for further illustration.

Unused percentage aims to evaluate the usage rate of adsorption reactor. Since the unused percentage usually cannot be higher than

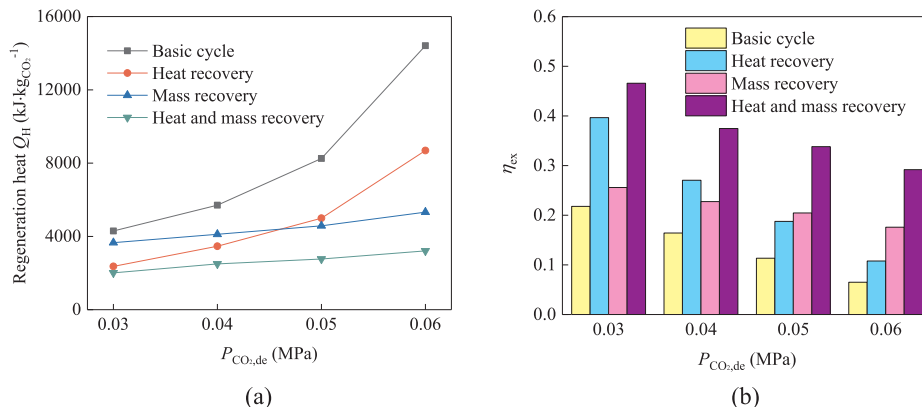


Fig. 6. Thermal performance of 4-step TSA cycles at different CO<sub>2</sub> partial pressures for desorption (a) regeneration heat; (b) exergy efficiency.

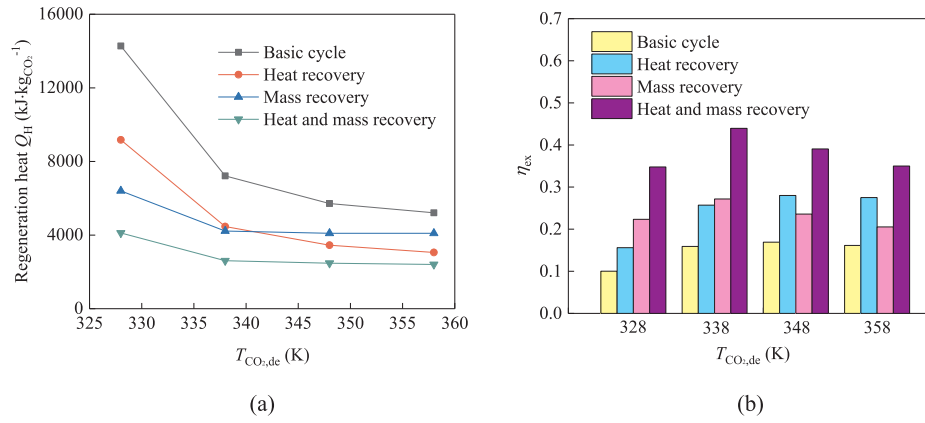


Fig. 7. Thermal performance of 4-step TSA cycles at different desorption temperature (a) regeneration heat; (b) exergy efficiency.

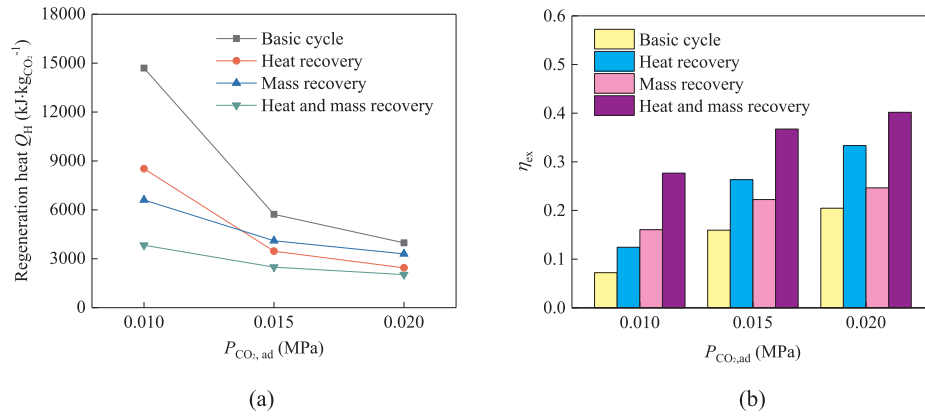


Fig. 8. Thermal performance of 4-step TSA cycles at different CO<sub>2</sub> partial pressure for adsorption (a) regeneration heat; (b) exergy efficiency.

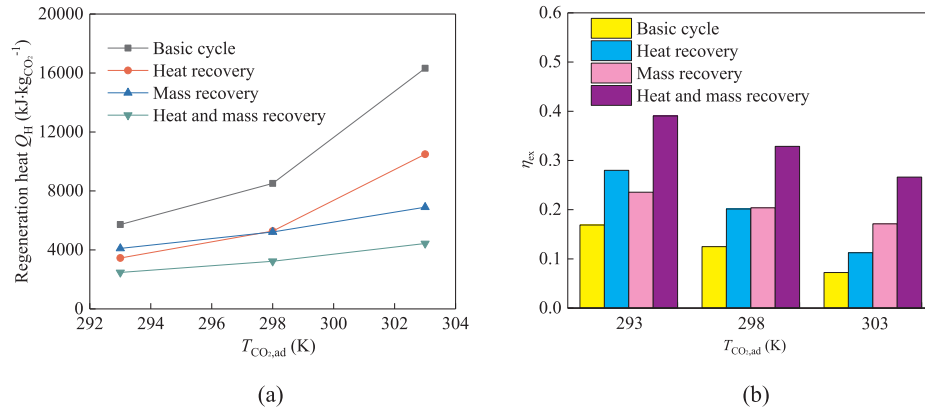


Fig. 9. Thermal performance of 4-step TSA cycles at different adsorption temperature (a) regeneration heat; (b) exergy efficiency.

40% [32], percentage of 0, 10%, 20% and 30% are selected for detailed comparison and further analysis, which could refer to Fig. 10. Fig. 10a indicates regeneration heat of the cycle in terms of different unused percentages of adsorption reactor. Results reveal that regeneration heat increases sharply with the increase of the unused percentage of the reactor since the working capacity declines and the excessive sensible heat input for unused part of reactor increases. Fig. 10b shows exergy efficiency of the cycle in terms of different unused percentages, which increases with the decrease of unused percentage. When the percentage increases from 0 to 30%, exergy efficiency ranges from 0.048 to 0.38. The improvement by using IHMR is up to 2.68 times in terms of different unused percentages. It is acknowledged that the unused part of the reactor cannot be avoided since it is strongly related to reactor

types, working conditions, filling methods, heat and mass transfer performance, etc. However, IHMR could improve the cycle efficiency by at least 2 times which would be more effective and prospective when unused percentage is increased.

According to Eq. (14), mass ratio is defined as the specific value between mass of sorption reactor and adsorbent. Exergy efficiency of 4-step TSA cycles in terms of different mass ratios is presented in Fig. 11. It is indicated that mass ratio has a remarkable influence on exergy efficiency due to the increased heat input of adsorption reactor. With the increased heat input of metal part, exergy efficiency decreases with the increase of mass ratio. When mass ratio increases from 0 to 8, exergy efficiency of a 4-step TSA cycle varies from 0.37 to 0.022. One remarkable fact is that the positive influence on exergy efficiency of the

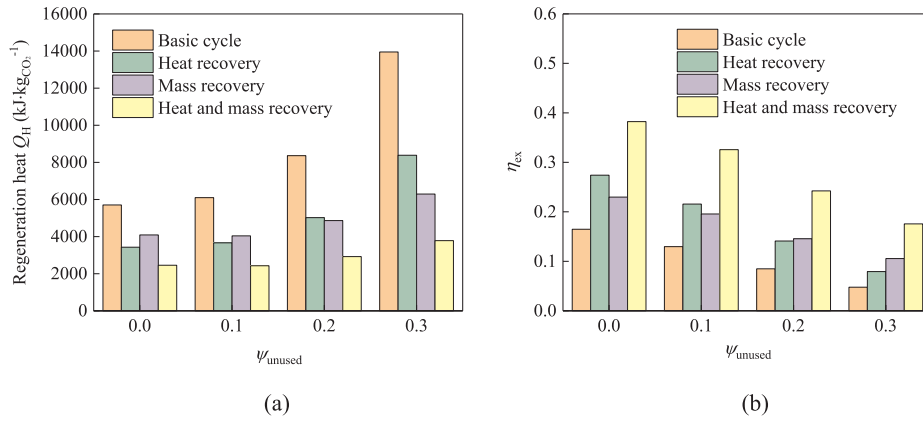


Fig. 10. Thermal performance of 4-step TSA cycles with regard to different unused percentages of adsorption reactor (a) regeneration heat; (b) exergy efficiency.

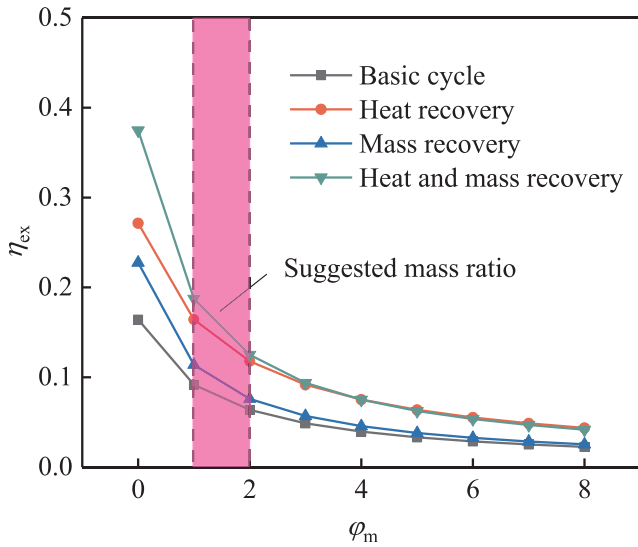


Fig. 11. Exergy efficiency of 4-step TSA cycles in terms of different mass ratios between adsorption reactor and adsorbent.

cycle is greatly reduced with the increase of mass ratio. When the mass ratio is higher than 4, IMR almost has no contribution on the improvement of exergy efficiency. This is because the high mass ratio results in the high regeneration heat input. It will significantly reduce the percentage of additional sorption capacity which makes IMR less meaningful. Under this scenario, the performance could be improved by only using the IHR. In real application, the mass ratio between adsorbent and adsorption reactor could be within 1–2 for post-combustion CCS system when compared with other adsorption applications e.g. adsorption cogeneration whose mass ratio is usually higher than 3 [33]. When the mass ratio is able to reach 2, the improvement of exergy efficiency by using IMR, IHR and IHMR could reach about 19.1%, 84.9% and 96.2%, respectively. It will become more desirable when the mass ratio is less than 2.

Fig. 12 indicates exergy efficiency of 4-step TSA cycles in terms of different mass recovery coefficients which could be affected by various factors e.g. pipe shape, valve type, recovery time, etc. It could be observed that mass recovery coefficient has no influence on the exergy efficiency of the cycle using IHR since no pressure potential could be recovered. When mass recovery coefficient varies from 0.5 to 1, exergy efficiencies of the cycle using IMR and IHMR increase from 0.198 to 0.229 and 0.328 to 0.382. Within this range from 0.5 to 1, the largest increment is no more than 20% which reveals that the improvement of mass recovery coefficient has a small influence on exergy efficiency of the cycle using IMR. Thus, IMR should be applied for a 4-step TSA cycle

in real application. However, there is no need to further optimise IMR by increasing the cost to use very high-quality valves and pipes though the suggested mass recovery coefficient is from 0.8 to 0.9 according to the common adsorption refrigeration mass recovery cycle [34].

#### 4.3. Further comparison and insight

In order to further illustrate different roles of recovery methods, exergy efficiencies of different post-combustion carbon capture technologies are first presented and different adsorption cycles are compared [27,35]. Fig. 13 indicates exergy efficiencies of different post-combustion CCS technologies when CO<sub>2</sub> concentrations of flue gas are between 10% and 15%. It reveals that different technologies have their up limits of exergy efficiencies for CO<sub>2</sub> capture. For cryogenics and other technologies, the efficiencies are generally lower than 10%. Sorption technologies e.g. adsorption and absorption are usually lower than 25% without using IHR/IMR. Exergy efficiency of membrane carbon capture technology could be a bit higher than 25% which is mainly determined by the materials. Fig. 14 shows exergy efficiencies of selected adsorption cycles i.e. TSA, VSA, pressure-temperature swing adsorption (PTSA) and electric swing adsorption (ESA) in terms of different recovery technologies when CO<sub>2</sub> concentrations range from 5% to 20%. The results of the basic cycle refer to the Ref. [36]. It can be observed that IHR is quite conducive to TSA and PTSA since the external heat is used for the desorption process of materials. VSA can only

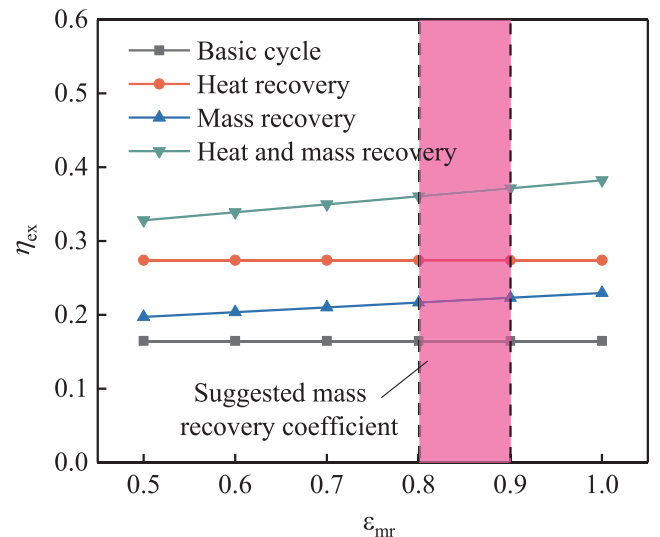


Fig. 12. Exergy efficiency of 4-step TSA cycles in terms of different mass recovery coefficients.



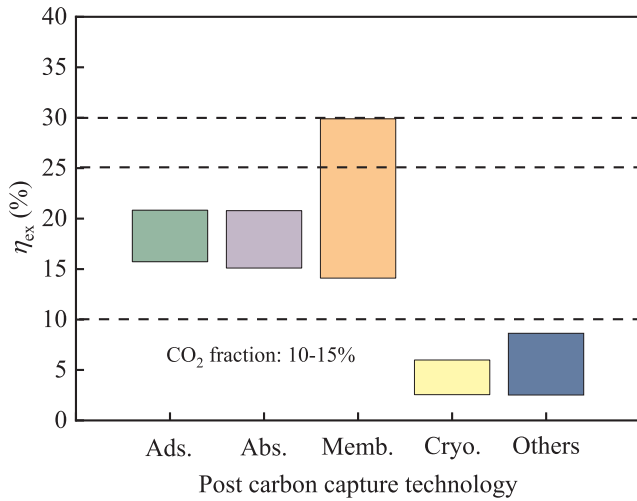


Fig. 13. Exergy efficiencies of various post-combustion CCS technologies [27,35].

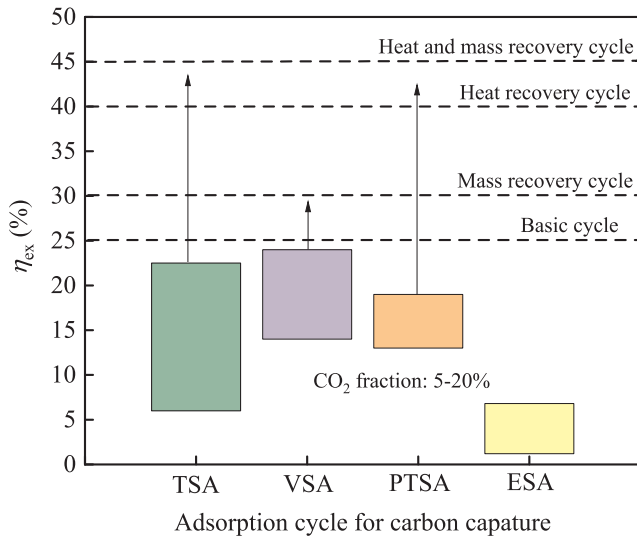


Fig. 14. Exergy efficiencies of the selected adsorption cycles in terms of different recovery technologies [36].

adopt IMR for performance improvement. No related recovery technology could be applied for improving the efficiency of ESA since it aims to improve other performance e.g. fast desorption rate. It is worth noting that up limits of exergy efficiencies of the selected adsorption cycles using IHMR could reach between 40 and 45%.

Table 1 comprehensively compares the recovery technologies for different adsorption CCS methods in terms of cycle candidate, more suitable condition, reactor, and improvement of exergy efficiency. It is demonstrated that IHR is more suitable for high desorption temperature and the improvement of up limit could reach at least 70% due to the large recovered heat. Comparably, IMR is better to be applied to the situation at low adsorption pressure. This is mainly because working capacity becomes much lower when adsorption pressure is low. Thus

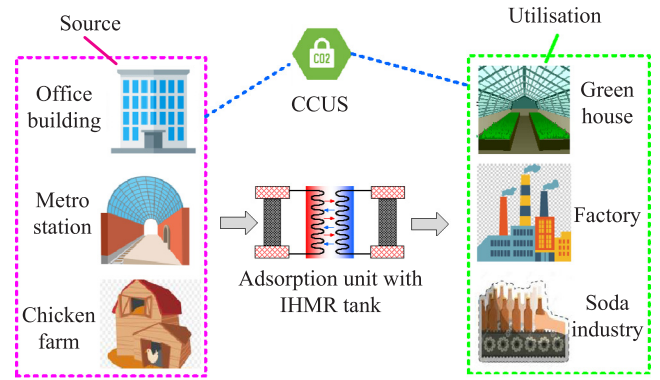


Fig. 15. Potential target application by using IHMR technology.

the up limit of exergy efficiency could be increased at least 24% when compared with that of basic cycle. The cost of the recovery technologies are mainly determined by the design for retrofitting the original systems [37]. Considering IHR, it lies in more heat exchangers required for recovering the sensible heat. Comparably, the additional cost of IMR depends on the valves and pipelines for adjusting the pressure difference.

Based on above characteristics of aforementioned recovery approaches for post-combustion carbon capture technologies, a potential target application is suggested in Fig. 15. That is direct air capture (DAC) with PTSA from places with high CO<sub>2</sub> intensity e.g. office building, hospital, farms in which CO<sub>2</sub> concentration is usually more than 500 ppm [38]. Adsorption unit is combined with the heat and mass recovery tank, which will be integrated with central air conditioning/ventilation system. Thus, the largest improvement could be achieved by using IMHR due to a relative low CO<sub>2</sub> concentration when compared with other sources e.g. power plant, iron and steel. The captured CO<sub>2</sub> could then be used for the roof greenhouse, factory, soda industry, etc.

## 5. Conclusions

4-step temperature swing adsorption cycles for CO<sub>2</sub> capture by using internal heat recovery, internal mass recovery as well as internal heat and mass recovery are evaluated based on carbon pump theory. The main parameters e.g. regeneration heat and exergy efficiency are determined based on characteristics of activated carbon. Unused percentage, mass ratio between adsorption reactor and adsorbent and mass recovery coefficient are adopted for analysing the performance in real application. Conclusions are yielded as follows:

- (1) The regeneration heat increases with the increase of desorption pressure and adsorption temperature while it increases with the decrease of desorption temperature and adsorption pressure. Exergy efficiency shows a reverse trend of regeneration heat. Recovery technologies have great influence on reducing regeneration heat for improving exergy efficiency. Through various recovery technologies, the highest exergy efficiency of 4-step temperature swing adsorption cycles could reach 0.465 at different desorption/adsorption temperature and pressure, which improves the efficiency up to 3.5 times compared with the performance of basic

Table 1

Comparison of different recovery technologies for sorption CCS cycles.

Item	Applied cycle	More suitable conditions	$\eta_{ex}$ improvement	Additional cost
IHR	TSA, PTSA	High desorption temperature	At least 70%	Heat exchanger
IMR	TSA, VSA, PTSA	Low adsorption pressure	At least 24%	Pipeline
IHMR	TSA, VSA, PTSA	No preference	At least 24%	Above two

cycle.

- (2) Unused percentage of adsorption reactor and metal ratio have large influence on the performance of adsorption cycles while mass recovery coefficient has a relatively small influence. When the unused percentage increases from 0 to 30%, exergy efficiency ranges from 0.048 to 0.38. IHMR could improve the cycle efficiency by at least 2 times which will be more effective when unused percentage is increased. Besides, when mass ratio increases from 0 to 8, exergy efficiency of the cycle varies from 0.37 to 0.022. When mass ratio is higher than 4, internal mass recovery almost has no influence on the improvement of exergy efficiency. When mass recovery coefficient varies from 0.5 to 1, the largest increment is no more than 20%.
- (3) Internal mass recovery is quite conducive to temperature swing adsorption and pressure-temperature swing adsorption while vacuum swing adsorption can only adopt internal mass recovery for performance improvement. The up limits of exergy efficiencies of adsorption cycles using internal heat and mass recovery could reach between 40 and 45%. Internal heat recovery is more suitable for high desorption temperature and its up limit of exergy efficiency could be improved by at least 70%. Comparably, internal mass recovery is better to be applied to the situation at low adsorption pressure with an improvement of at least 24%.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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